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ALUMINUM-CHLORINE BATTERY

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ABSTRACT

During the present report period the feasibility of the chlorine cathode in $AlCl_3$-NaCl-KCl eutectic electrolyte has been studied. Investigations on vitreous carbon electrodes have shown that carbon is intrinsically active for chlorine reduction in $AlCl_3$-alkali chloride eutectics. A study of compatibility of carbon electrodes for chlorine in $AlCl_3$-eutectics has uncovered carbon samples which appear suited for the construction of porous chlorine cathodes. In addition, a method has been developed to obtain very pure $AlCl_3$.

CONTENTS

INTRODUCTION

The present work is concerned with demonstrating the feasibility of a battery composed of an Al negative and a Cl_2 positive in a low temperature molten electrolyte of $AlCl_3$-NaCl-KCl. The operating temperature of this system would be in the range 120 to 150°C, with a theoretical energy density of 650 watt-hr/lb.

In addition to demonstrating the feasibility of this kind of battery, it is our aim to optimize it and to define its limitations by determining the kinetic parameters of the electrodes and the pertinent physico-chemical data of the electrolyte.

In a previous report[1] experimental work directed towards the understanding of the electrochemistry of the aluminum electrode was given. This work not only showed the feasibility of using this electrode for the planned battery, but also indicated some of the intrinsic limitations of this electrode, e. g. the presence of passivation which will have to be studied at a later date.

During the present report period, work has been directed toward studying the feasibility of the chlorine electrode. This includes (a) an exploratory study of the intrinsic activity of smooth carbon electrodes for chlorine reduction and (b) a study of the compatibility of carbon substrates to both chlorine in an $AlCl_3$-NaCl-KCl eutectic and to the electrolyte itself. In addition, work has been directed toward the development of a standard method of producing pure aluminum chloride which would allow us to obtain unambiguous data when studying the electrode reactions and the physico-chemical properties of the melt itself.

PURIFICATION OF $AlCl_3$

Previous work has shown that commercially available $AlCl_3$, even of the purest grade, has considerable amounts of impurities. These impurities are reflected in the presence of peaks in the cyclic voltammetry curves, some of them attributable to the presence of iron. In addition, the melts, as prepared, show a brownish coloration the intensity of which increases with time.

The change of coloration may be due to (1) the formation of colloidal hydroxides of heavy metals as the melt adsorbs water, (2) to a higher degree of oxidation of these impurities, or (3) to decomposition of organic material. Thus, in order to obtain satisfactory clean eutectics we have studied first the behavior of a large number of electrolytes prepared with several $AlCl_3$ samples obtained from different manufacturers. Eutectics with composition $AlCl_3$-NaCl-KCl, 66-20-14 mol % have been prepared using 10 $AlCl_3$-samples (Mallinckrodt Lot RTY and Lot TJB; Fisher Lot 780679; MCB Lot 25; Baker and Adamson Lot B128; J. T. Baker Lot 33025 and Lot 33824; BDH (Gallard-Schlesinger, N. Y.) Lot 0564110; Fluka (Buchs, Switzerland) Lot 461085; Koch-Light Labs (Colnbrook, Buckinghamshire, England)).

In all cases at 120°C the eutectic showed the brownish discoloration, which was lightest in the case of the Fluka material. Therefore, it was decided to start with this material when attempting to develop a standard purification technique.

Partial success in the purification of this material has been seen in previous work after treatment of the final eutectic with aluminum turnings. The success is not complete, since the effectiveness of this treatment varied from case to case. After postulating that an aluminum oxide layer is responsible for the lack of consistency in the degree of purification, we attempted to solve this problem by using an amalgamated aluminum plate which was kept under stirring in the eutectic for 6 hours. This treatment succeeded in removing the coloration and in substantially decreasing the iron peaks of the cyclic voltammetric curves. However, a small peak at a potential of about 1.5 v was introduced which can be attributed to the presence of Hg^{++} in solution.

Pre-electrolysis of the eutectic at 120°C for 24 hours using Ultra Carbon U-5 grade carbon electrodes was successful in decreasing the iron peaks but did not improve the coloration sufficiently.

After these preliminary purification attempts yielded erratic results, it was decided to adopt the following method, which was found to give the most satisfactory results, as standard procedure: $AlCl_3$ is mixed with sodium chloride and potassium chloride in the ratio of about 1.0 mols KCl, 1.5 mols NaCl, and 9.8 mols $AlCl_3$ giving a liquid at ~ 130°C with a high $AlCl_3$ vapor pressure. This liquid is treated with magnesium turnings to ensure the precipitation of such impurities as iron chloride which show an apparent appreciable vapor pressure. From this melt aluminum chloride is evaporated at a constant temperature of 215°C and condensed as large crystals in the cold part of the apparatus. By using two 1 liter resin reaction kettles as shown in Fig. 1, about 70 grams of pure $AlCl_3$ can be obtained overnight. Figure 2 shows the crystallized material in the upper part (cold part) of the apparatus. The material seems to be clean as evidenced by its clearness, the production of virtually transparent eutectics, and the lack of any residual current in the cyclic voltammetric curves obtained with said eutectics.

STABILITY OF CARBON ELECTRODES

Our preliminary investigation has shown that aluminum chloride eutectics attack porous carbon electrodes with some degree of graphitization. This attack is more pronounced in the presence of chlorine. We have now extended the study of the compatibility of carbon electrodes from different sources and of different degrees of graphitization and porosity with respect to aluminum chloride eutectics, both in the presence and the absence of chlorine. For these experiments, a $AlCl_3$-NaCl-KCl eutectic (66, 20, 14, mol %) at 120°C was used. When investigating the effect of chlorine, the carbon electrode was partially immersed in the electrolyte and chlorine was passed through the gas phase of the all-glass cell. The results of these preliminary experiments are presented in Table I.
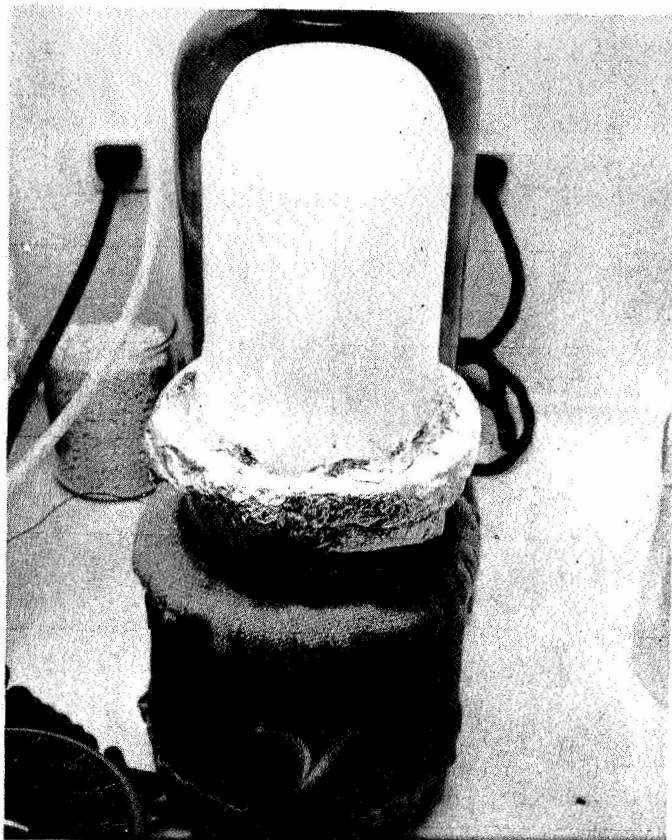
Fig. 1   AlCl$_3$ purification unit (in inert atmosphere chamber).

Fig. 2 View of condensed AlCl$_3$-crystals in cold part of purification unit.

TABLE I.   Stability of Carbon/Graphite Materials in AlCl$_3$-NaCl-KCl-Eutectic in Absence and in Presence of Chlorine

Material Identification	Source	Conditions		Remarks on Cl$_2$-Effect
		AlCl$_3$ eut. at 120°C	w/Cl$_2$ passed over melt	
#37 porous carbon	Speer Carbon	no attack	no attack	in contact over 48 hrs.
p-6038-C carbon-graphite	Pure Carbon	"	failed	failed in less than 15 min.
PO2 dense carbon	"	"	no attack	
103G dense graphite	Speer Carbon	"	failed	failed in less than 10 min.
104 dense graphite	"	"	"	failed in less than 10 min.
108 dense carbon-graphite	"	"	"	failed in less than 10 min.
37G porous graphite	"	"	"	failed in less than 30 min.
Graphitite "A"	Carborundum	failed	"	rapid failure
L-50 porous carbon-graphite	Pure Carbon	no attack	"	failure in 10-15 min.
L-56	"	"	"	failure in 10-15 min.
PO3	"	"	"	failure in 10-15 min.
P3W	"	"	"	failure in 10-15 min.
CS grade dense graphite	National Carbon	"	"	failed in less than 30 min.
Vitreous carbon	Atomergic-Chemetals	"	no attack	no attack after more than 72 hrs. contact w/AlCl$_3$
Pyrolytic graphite	Ultra Carbon	"		Pyrolytic graphite coating a piece of plain graphite – appears to have resistance to attack

This table shows that deterioration, as evidenced by the swelling or erosion of the surface, is much more evident in presence of chlorine, only in the case of a few graphite samples did substantial swelling occur in absence of chlorine. Furthermore, corrosion by Cl_2 is very much more pronounced in samples with some graphite content than in carbon samples without graphite. The samples which resisted corrosion are a Pure Carbon PO2 sample which is a high density carbon and a Speer carbon sample (#37) which is a porous carbon with little graphite content. Vitreous carbon from Atomergic Chemetals, did not show any deterioration, even after observation of the interface under the microscope. It also seems possible that pyrolytic graphite may show sufficient compatibility to the $Cl_2/AlCl_3^-$ eutectic environment. As a consequence of this work, we intend to use the #37 Speer carbon material to determine the feasibility of a carbon based chlorine diffusion electrode and Pure Carbon PO2 as construction material when a high density impermeable carbon is required. Vitreous carbon will be used for kinetic studies of the chlorine reduction on smooth carbon surfaces; some preliminary results are described in the following section.

REDUCTION OF CHLORINE ON SMOOTH VITREOUS CARBON ELECTRODES

While trying to develop porous carbon electrodes compatible with a $Cl_2/AlCl_3$ eutectic system, we investigated the intrinsic activity of pure vitreous carbon for chlorine reduction in the $AlCl_3$-NaCl-KCl eutectic Since at the time no $AlCl_3$ with sufficient purity was available, it was decided to minimize the effect of impurities by working with partially immersed smooth electrodes so as to study the reduction of chlorine at the meniscus representative of the 3-phase boundary of a porous gas diffusion electrode[2]. For these experiments, a rod of vitreous carbon of 0.3 cm diameter from Atomergic Chemetals Corporation was used. This carbon has a highly disordered structure which, coupled with a

very high density, makes it very resistant to attack by chlorine in $AlCl_3$ eutectics. Another interesting feature of this material is its expansion coefficient which allows us to make very good seals to borosilicate glass. The electrolyte was the $AlCl_3$-NaCl-KCl eutectic which was used (unless otherwise stated) at a temperature of 120°C. Aluminum was used as both reference and counter electrodes. The electrolyte was saturated with argon and the chlorine gas was passed above the electrolyte level.

In an experiment with a half immersed electrode of 2 cm length, an open circuit potential of 2. 1 v vs. Al electrode was obtained. Starting from this potential the potentiostatic current-potential curve of Fig. 3 was obtained in which each point was measured after waiting 5 minutes. To demonstrate that the current was produced by chlorine reduction on carbon, chlorine was replaced by argon and the decay of current at constant potential recorded as a function of time as shown in Fig. 4. After renewed introduction of chlorine, the current increased again to a value close to the previous value. The delay in reaction to gas changes can be easily explained by the gas volume in the electrochemical cell and tubings. The effect of potential on current was further investigated, as shown in Fig. 5, by following the current as a function of time of constant potential.

Figure 5 shows that while the currents are rather stable at the low polarizations, larger fluctuations occur at increasing polarizations. These are probably due to the effect of the increasing depth of penetration of the Cl_2-reduction along the thin film with increasing polarization, and the resulting sensitivity of the results to convection and to drying out of the film.

In general, the results reported here can be considered only as semi-quantitive since the film is not well-defined due to the mentioned changes caused by convection or drying out of the film. However, these results can be interpreted as clear proof that pure carbon is intrinsically active in catalyzing the reduction of Cl_2 in $AlCl_3$-NaCl-KCl electrolytes.
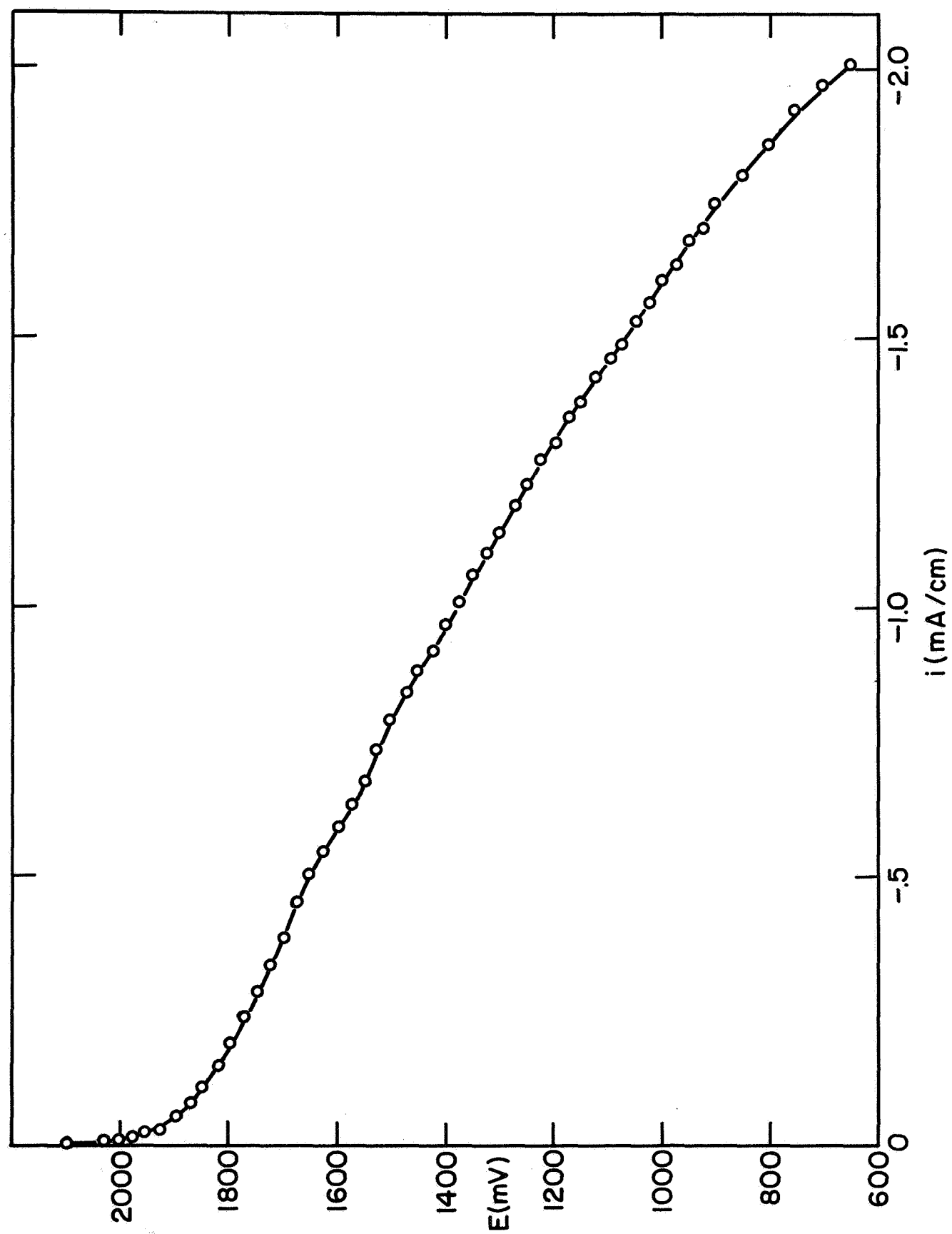
Fig. 3   Potentiostatic current-potential curve for Cl_2-reduction on partially immersed vitreous carbon electrode
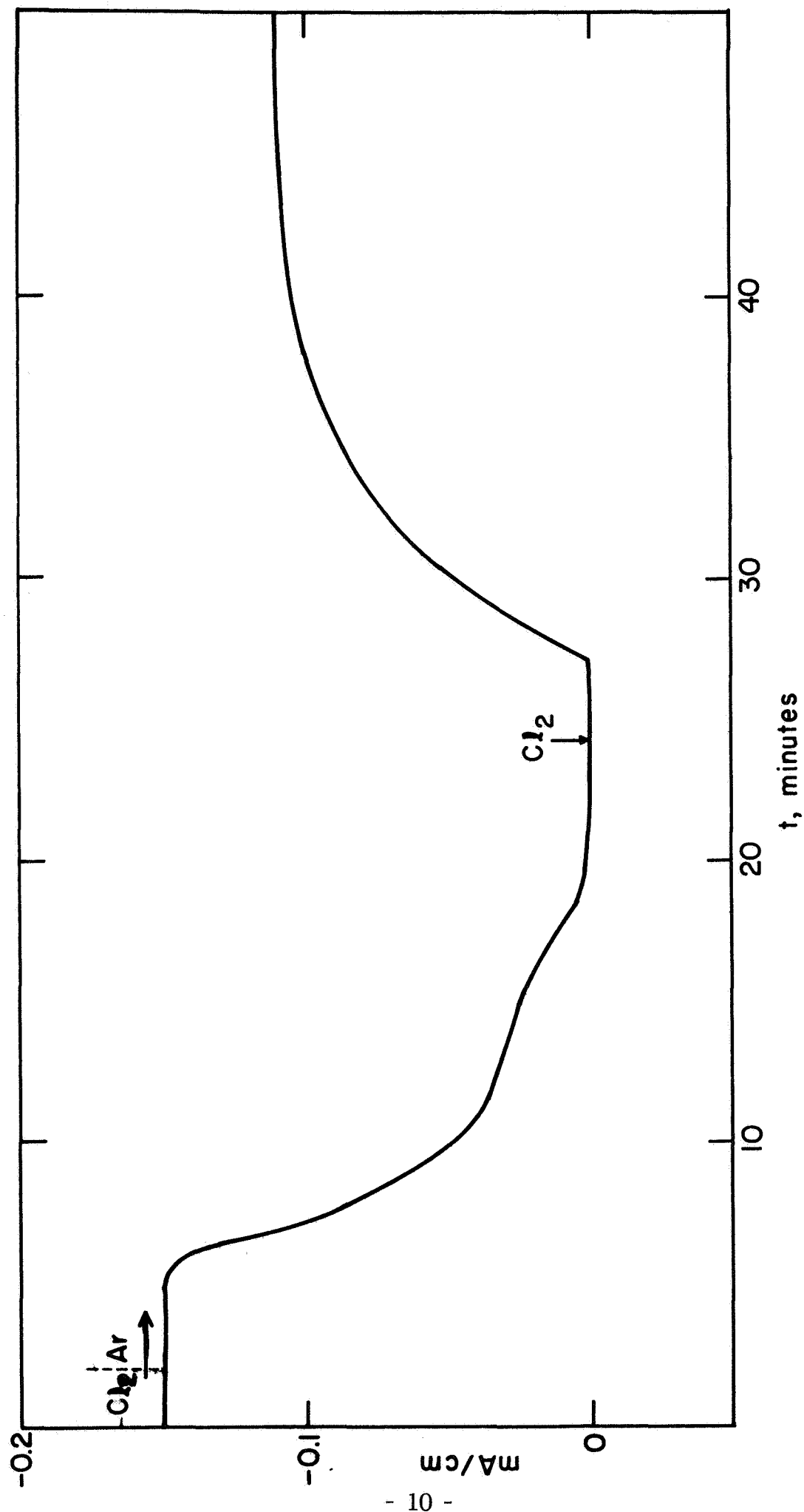
Fig. 4 Effect of Cl$_2$-gas on current obtained with partially immersed vitreous carbon electrode, potentiostated at 1. 8 volt (vs. Al-reference electrode).
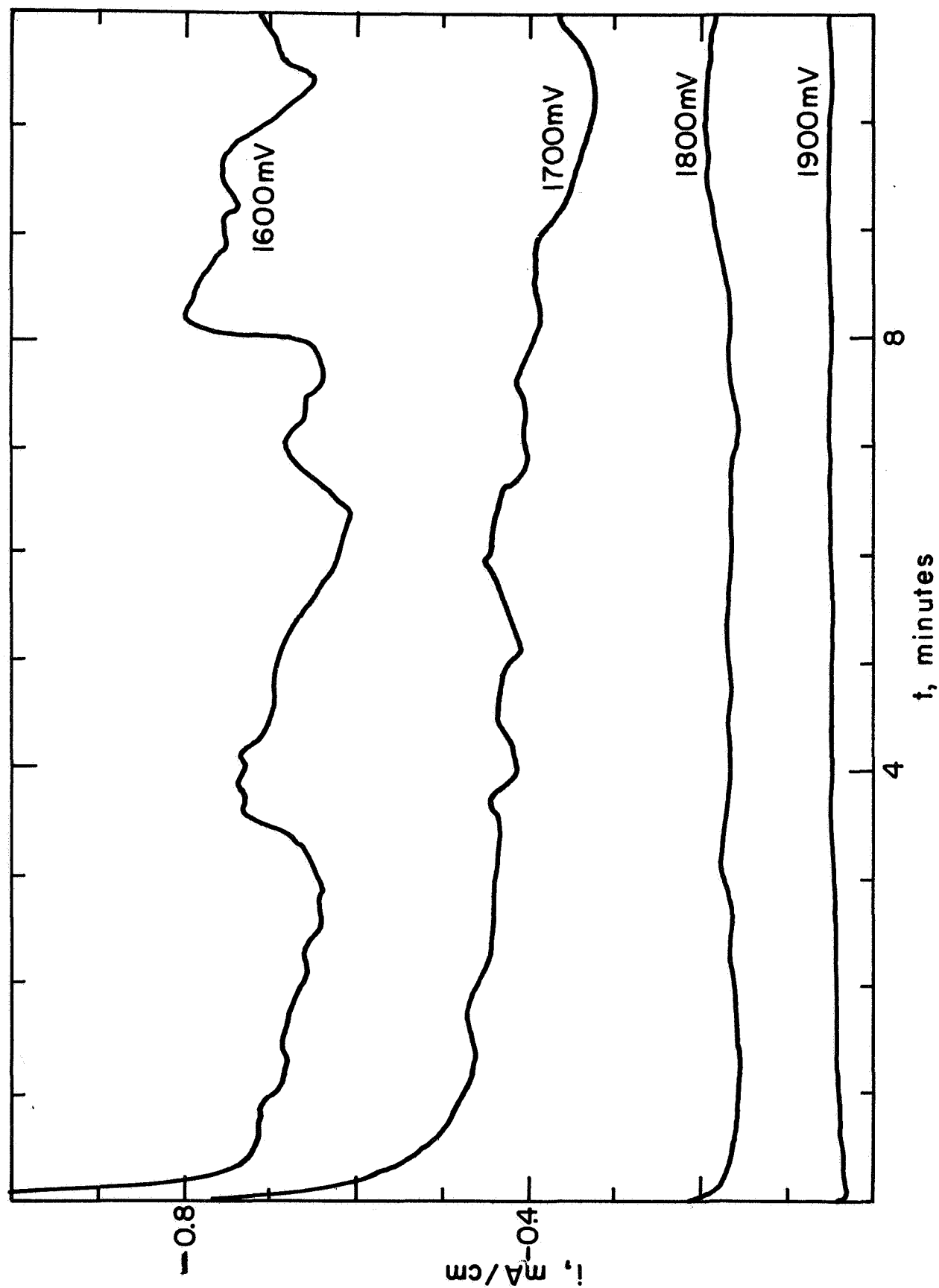
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Fig. 5   Effect of potential on potentiostatic current-time curves for Cl_2-reduction on partially immersed vitreous carbon electrode.

A series of tests were carried out to determine the contribution of the immersed part of the electrode in producing the current in an experiment in which the stagnant electrolyte had been saturated with chlorine. This experiment did show that there was no decrease in current when the immersed part of the electrode was reduced practically to zero. Another series of experiments performed to approximately establish the effective length of the meniscus (and thin film) showed that reduction of the immersed part of the electrode down to 0.2 cm did not substantially affect the magnitude of the current.

In order to ascertain the effect of electrode pretreatment, the electrode was anodically polarized for 0.2 minutes to evolve chlorine at a current density of +0.5 ma. After this pretreatment, the activity for chlorine reduction of the carbon as a partially immersed electrode was substantially unchanged. The same was true after cathodically polarizing the electrode for 0.1 minutes at 1000 mv potential.

In another experiment the flow of chlorine was greatly increased above the electrolyte surface; this resulted in an increase of the current which could be attributed to either a drying out of the film or to an increase of the chlorine partial pressure at the interface with the film. This experiment showed that in order to use this type of data for quantitative measurements, extreme care should be taken in controlling the gas phase concentration with respect to chlorine and $AlCl_3$ vapor.

To compare the activity of carbon with that of platinum, two experiments were carried out in the same melt and under the same conditions, using first a carbon electrode and then a platinum electrode with the same degree of immersion. The results, given in Fig. 6. show an over-all higher activity of platinum vs. that of carbon. The fact that the open circuit of the platinum electrode is about 60 mv lower than that of the carbon electrode can be construed as an indication of corrosion of the platinum electrode at the theoretical potential of the chlorine electrode.
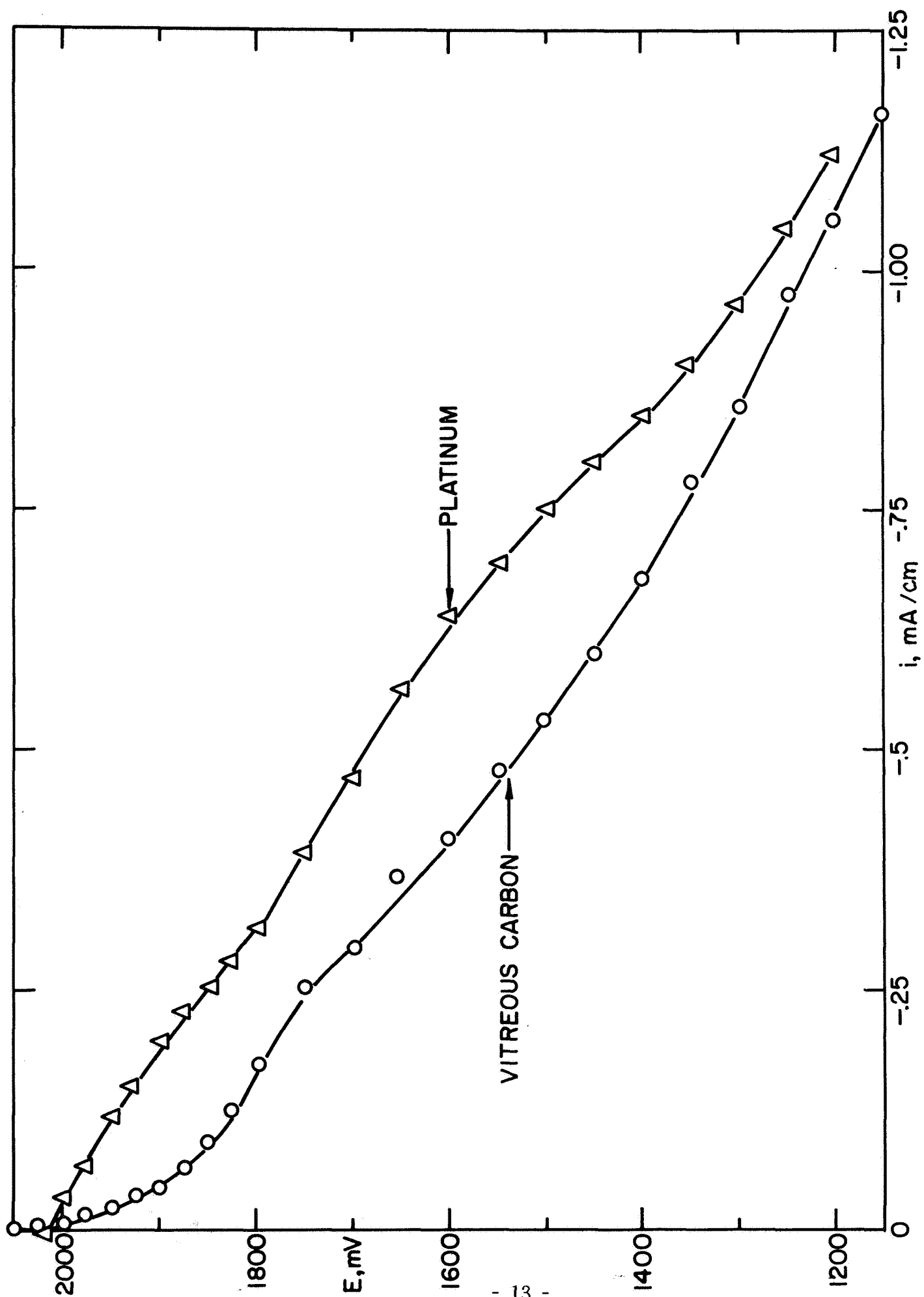
Fig. 6   Comparison of i-E-curves for Cl_2-reduction on partially immersed platinum and vitreous carbon electrode.

In summary, the work with partially immersed vitreous carbon electrodes indicates that carbon has enough intrinsic activity to warrant the testing of an unactivated porous carbon electrode as chlorine cathode in the $AlCl_3$-NaCl-KCl eutectic. In addition, the experience with vitreous carbon electrodes show that this material should be ideally suited for studying the reduction kinetics of the dissolved chlorine using a rotating disc and a stationary electrode when very pure $AlCl_3$ eutectics are available.

CONCLUSIONS AND FUTURE WORK

Investigations on vitreous carbon electrodes have shown that carbon is intrinsically active for chlorine reduction. In addition, the study of compatibility of carbon materials for chlorine electrodes in $AlCl_3$-eutectics has uncovered carbon samples which appear suited for the construction of chlorine cathodes for operation in this electrolyte.

Work in the immediate future will be directed towards demonstrating the feasibility of chlorine cathodes using porous gas diffusion carbon electrodes, by constructing and operating these electrodes. Since in the previous report we have established the feasibility of the aluminum anode, the next step will be to establish the feasibility of the complete Al/Cl_2 battery and to define in the first approximation its discharge characteristics.

To optimize this battery further, and to establish with accuracy its limits of operation, it is planned to study the kinetic parameters of both electrodes and the pertinent physico-chemical data (phase diagram and conductivity) of $AlCl_3$-electrolytes. This work has now been made feasible by the development of a standard method to obtain pure $AlCl_3$ in sufficient amounts.

REFERENCES

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2. F. Will, J. Electrochem. Soc. 110, 145 (1963).